THE ROLE AND SIGNIFICANCE OF THE COMPLEX ANIONIC POTENTIALS IN THE GEOCHEMISTRY

Part V. The periodicity of the complex anionic potentials

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1. INTRODUCTION

Szádeczky-Kardoss (1955) in his book „Geochemistry" dealing briefly with the connection between the ionic potentials of the complex-forming cations and their complex oxyanions states that the complex anionic potentials decrease as the corresponding cationic potentials increase within the same period whereas in the same groups of the periodic table both the complex anionic potentials and the cationic potentials decrease by increasing the number of the periods.

Grasselly has also dealt with (1959a) the connection between the ionic potentials and the corresponding anionic potentials attempting to characterize the stability relations of tetrahedral oxyanions on the basis of their complex anionic potentials.

On the basis of results of the studies of recent years relating to the complex-anionic potentials introduced in the geochemistry by *Szádeczky-Kardoss* (1954), it seems to be expedient to examine in detail how the complex anionic potentials change in the periodic system, and further what conclusions may be drawn from the periodicity of the complex anionic potentials.

2. THE CHANGE OF THE COMPLEX ANIONIC POTENTIAL IN THE PERIODIC TABLE

Denoting in the Periodic Table the ionic potentials of the complex-forming cations, the corresponding complex anionic potentials, the electrostatic energies of the complexes computed from ionic model as well as — if data were available — the energy constants according to *Huggins* and *Sun* (1946), it can be clearly observed that in the single periods the ionic potentials on the whole increase from left to right and correspondingly decrease the complex anionic potentials, whereas

vertically, in the single groups of the Periodic Table both the ionic potentials and the complex anionic potentials decrease downwards. Exception can only be established in the relation of the series of Zr^{4+} — Nb^{5+} — Mo^{6+} and Hf^{4+} — Ta^{5+} — W^{6+} owing to the lanthanide contraction. Both the cationic potential of the Hf an Ta and the complex anionic potentials of their corresponding tetrahedral complexes are higher than they would be expected taking into consideration the generally downward revealing decreasing tendency of both values. In the case of Mo^{6+} and W^{6+} the corresponding values are the same, that is the ionic potential of both the Mo^{6+} and the W^{6+} is 10,34 and the complex anionic potential of the MoO_4^{2-} and the WO_4^{2-} anions, respectively, is 0,59.

Within the single periods neither the increase of the cationic potentials from left to right nor the decrease of the corresponding complex anionic potentials in the same direction are continuous during the whole period. For example, in the period 4, in the series of Ti—V—Cr—Mn placed before the iron-group, the ionic potential continuously increases and correspondingly decreases the complex anionic potential. The same can be stated in the series of Ga — Ge — As — Se placed in the same period but after the iron-group. However, between the two series, although both belong to the same period, the change of the cationic potentials and the complex anionic potentials, respectively, is not continuous.

Using the short-period form of the Periodic System the evidence of the change of the cationic potentials and the complex anionic potentials, respectively, is interferred especially vertically because in the single groups the elements of the subgroups are included and the most closely related elements are not always successively followed.

The change of the potentials is more clearly visible in the form of the periodic table used by *Fersman* wherein beneath the elements of the series Al — Si — P — S — Cl really the most closely related elements of the series Ga — Ge — As — Se — Br are placed and in the right side of that table beneath the elements of the series Ti — V — Cr — Mn directly follow the most closely related elements of the series Zr — Nb — Mo as in this form of the periodic table the elements of the subgroups — included in the short-period form by the single groups — are separated.

To demonstrate clearly the change of the values mentioned is especially advantageous the form of the Periodic Table according to *Szabó* and *Lakatos* (1954) including also the peculiarities of the *Fersman*'s table.

In this system the elements of the *Mendeleev*'s periods do not get into the same horizontal rows as the periodicity is associated with the periodicity of the shell structure and each row represents the completion of the single shells (except the alkalies and the alkali earth metals) as it is stated by these authors. In this system the subgroups are separated from one an other as in the *Fersman*'s table. The separation of the subgroups, the clear demonstration of the horizontally and vertically relationships among the elements by this system offer the possibility of

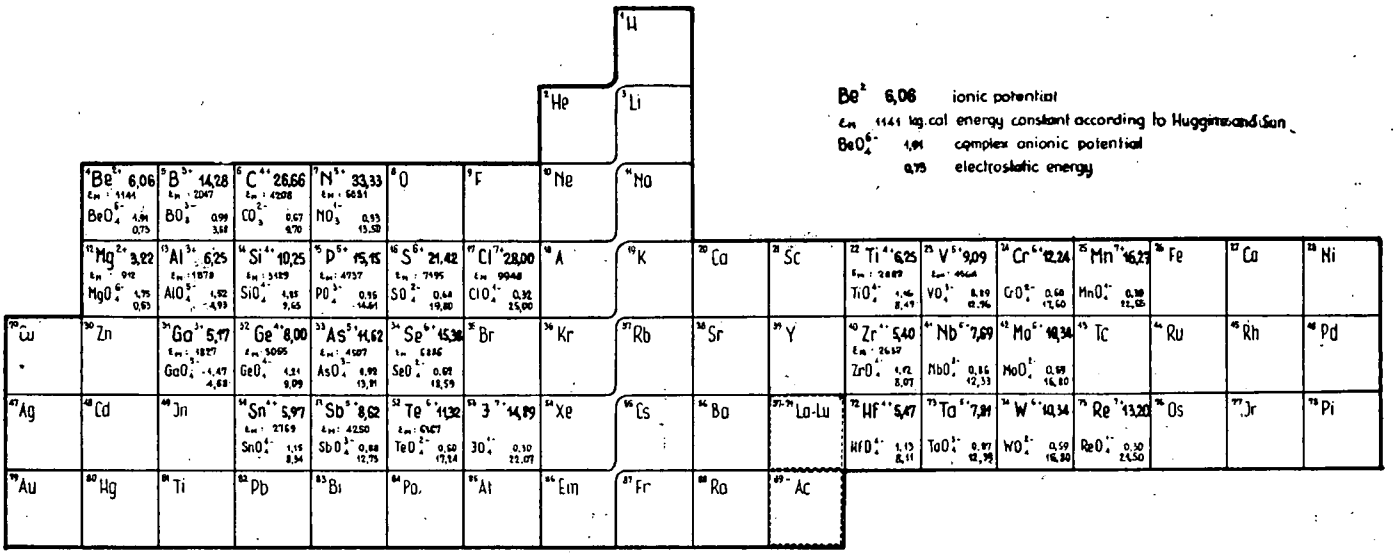

Fig. 1. Ionic potentials and energy constants of complex-forming cations as well as the complex anionic potentials and electrostatic energies of the corresponding tetrahedral oxyanions in the periodic table according to *Szabó* and *Lakatos*

a more distinct study of the change of ionic potentials and the complex anionic potentials as well as that of the energy constants and the electrostatic energies in the periodic table.

3. CONNECTION BETWEEN THE ELECTROSTATIC ENERGIES AND THE ANIONIC POTENTIALS OF THE TETRAHEDRAL COMPLEX OXYANIONS

Dealing with the stability relations of the complex oxyanions to characterize these stability relations the author *(Grasselly,* 1959a) has used the electrostatic energies computed from simple ionic model and expressed in arbitrary units. The anionic potentials and the electrostatic energies of the different complex anions are included in Table 1.

Table 1.

Complex anion	ψ_{MO_4}	U_{MO_4}	Complex anion	ψ_{MO_4}	U_{MO_4}
MgO_4^{6-}	1,75	0,63	VO_4^{3-}	0,89	12,96
BeO_4^{6-}	1,91	0,73	AsO_4^{3-}	0,92	13,81
GaO_4^{5-}	1,47	4,68	PO_4^{3-}	0,95	14,61
AlO_4^{5-}	1,52	4,93	MoO_4^{2-}	0,59	16,80
ZrO_4^{4-}	1,12	8,07	WO_4^{2-}	0,59	16,80
HfO_4^{4-}	1,13	8,11	TeO_4^{2-}	0,60	17,24
SnO_4^{4-}	1,15	8,34	CrO_4^{2-}	0,60	17,60
TiO_4^{4-}	1,16	8,47	SeO_4^{2-}	0,62	18,59
GeO_4^{4-}	1,21	9,09	SO_4^{2-}	0,64	19,80
SiO_4^{4-}	1,25	9,65	ReO_4^{1-}	0,30	21,50
NbO_4^{3-}	0,86	12,33	JO_4^{1-}	0,30	22,07
TaO_4^{3-}	0,87	12,39	MnO_4^{1-}	0,30	22,55
SbO_4^{3-}	0,88	12,76	ClO_4^{1-}	0,32	25,00

The connection between these values is illustrated in Fig. 2. The connections clearly shown in Fig. 2 as well as the conclusions to be drawn, emphasize the geochemical importance of the complex anionic potentials and the possibility of their manifold applications for interpretation of various geochemical problems.

From Fig. 2 the following may be concluded:

a) The connection between the complex anionic potentials and the electrostatic energies characterizing the stability relations of the tetrahedral oxyanions is linear.

b) The stabilities of the complex anions arranged along the lines from left to right downwards increase by decreasing complex anionic potentials.

c) The successive series beneath each other of the cations of complexes found on the lines going downward from left to right represent the single

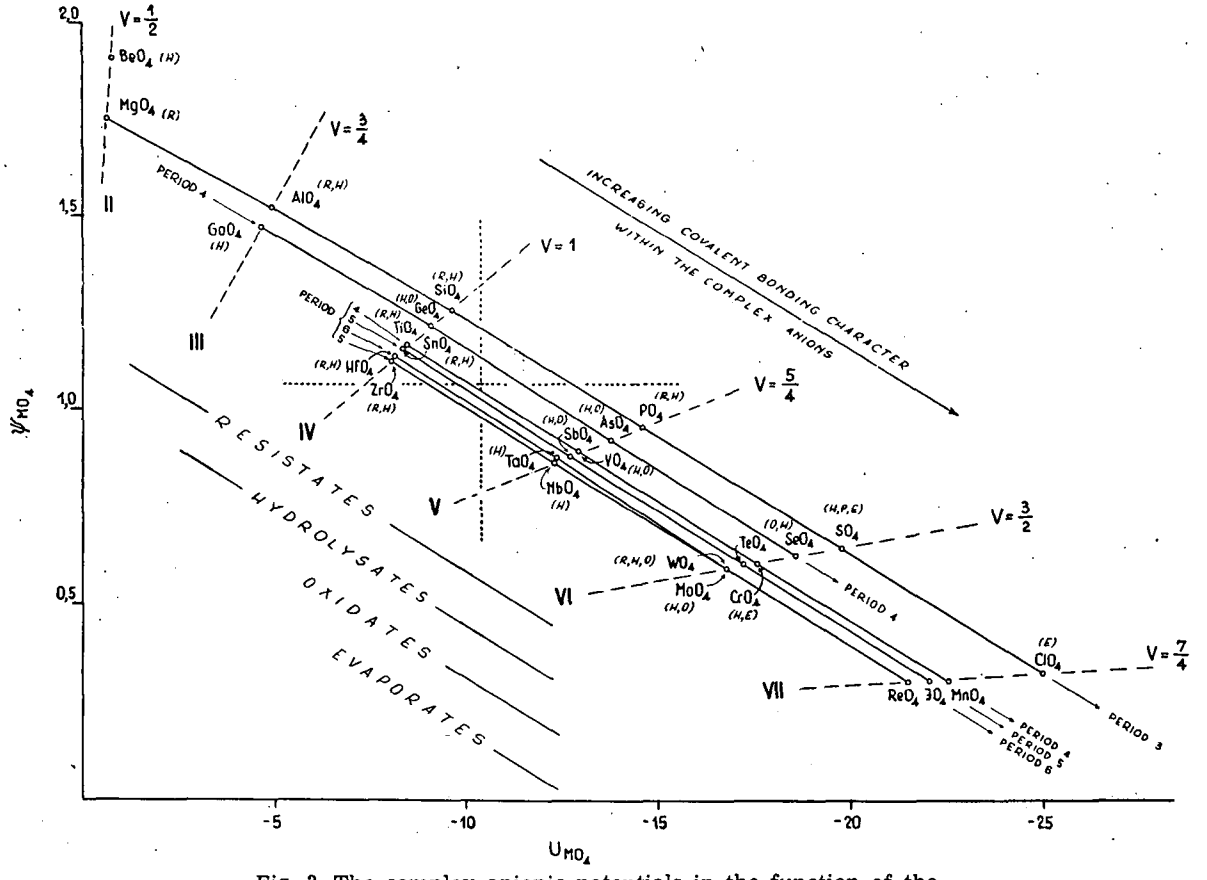

Fig. 2. The complex anionic potentials in the function of the electrostatic energies

periods and the halves of the periods, respectively. The uppermost line would represent (apart from Be as from the period 2 it is only alone taken into consideration, however, calculating the anionic potential and the electrostatic energy, respectively, of the BO_4^{5-} too, the point denoting the place of this anion in Fig. 2 would be placed as expected) the period 3, whereas the two lines beneath it would correspond to the two halves of the period 4, under the elements of the period 3 follow directly the closely related elements of the period 4 that is the Ga, Ge, As, Se and on the third line the other elements of the period 4 are arranged, that is the Ti, V, Cr, Mn and their corresponding complexes, respectively. The following line represents the one half of the period 5 and again such elements succed firstly which are more closely related to the Ge, As, Se, that is the Sn, Sb, Te. Theoretically the elements of the other half of the period 5 would follow but owing to the lanthanide contraction the next line, determined by Hf, Ta, W and Re, represents the period 6 and on the last line representing the other half of the period 5 are placed the Zr, Nb and Mo and their corresponding complexes, recpectively. The lines representing the two periods at the W and Mo, respectively, coincide, since the charges of the two ions are equal and their radii are also identical due to the lanthanide contraction. Thus the Fig. reflects also the effect of the lanthanide contraction.

d) In the Fig. 2 the single groups of the periodic table similarly can be well distinguished. The stabilities of the complexes within each group increase by increasing complex anionic potentials from left to right upwards. This increase in the given direction is generally joined with the decrease of the number of periods (except the exchange of the period 6 and the one half of the period 5 mentioned above). This Fig. proves evidently that the complex anionic potentials are suitable to characterize the stability relations of complexes of elements belonging to different periods or groups of the periodic table as it has been pointed out by the author *(Grasselly,* 1959a).

e) Considering the chemical and crystallochemical peculiarities of the complexes enumerated, approximately two groups of the complexes may be distinguished in the Fig. The boundary between the two groups would be drawn about at $\psi_{MO_4} = 1{,}00$ and $U_{MO_4} = 10$—12 values, respectively. The complex anions of lower anionic potential than 1 and of higher electrostatic energy than 10 in general are stable and in aqueous solution too, are present as complexes and are not dissociated to ingredient ions and generally are the characteristic components of anisodesmic structures with considerably strong covalent bonding character as for example the ClO_4^{1-}, SO_4^{2-}, CrO_4^{2-}, AsO_4^{3-}, PO_4^{3-}, WO_4^{2-}, MoO_4^{2-} ions. On the other hand, the complex anions with anionic potential higher than 1 and with electrostatic energy lower than 10 are no longer so stable, in silicate melts, however, can be present as independent tetrahedral complexes. Some of these complexes exist also in crystals as real tetrahedral oxyanions, e. g., the SiO_4^{4-}, AlO_4^{5-}, GeO_4^{4-} as components of mesodesmic structures.

The differences in the bonding character and consequently in the peculiarities of the anions belonging to the two different groups are

shown also by the fact that in crystals, e. g., the SO_4^{2-}, WO_4^{2-}, SiO_4^{4-}, anions can be equally considered as real complex anions in physical sense, however, in aqueous solution at least the SO_4^{2-} and WO_4^{2-} ions occur, whereas the SiO_4^{4-} anion do not, although in silicate melts such anions also exist.

It is to note further that supposing only conditionally the existence of LiO_4, NaO_4 „complex anions" and computing their „anionic potentials", as well as electrostatic energies, the points determined by this values would get in the Fig. on the left side of the ψ axis which indicates that such complex anions can not exist and if such tetrahedra should occur in some crystals, they are complexes merely in geometrical sense but can not be considered as real complex anions in physical sense.

Matossi and *Krüger* (1936) have investigated among others the infrared reflection spectra of the Li_2WO_4 and the Be_2SiO_4. The two compounds from crystallographical viewpoint are isomorphous, the WO_4 groups corresponds to the SiO_4 groups and the LiO_4 tetrahedra existing in the structure of the Li_2WO_4 are formally analogous with the BeO_4 tetrahedra of the latter compound. In the infrared spectra, however, only the active vibration of short wave length of the WO_4 groups was to be detected, whereas that of expected for the LiO_4 tetrahedron was missing.

Consequently the authors mentioned have stated as follows: „Es ist zu bedenken, dass die SiO_4- Tetraeder einen ganz anderen Bindungsmechanizmus bezüglich leichter Ionen aufweisen als die WO_4- Gruppe, was ja schon die Tatsache zeigt, dass in Lösungen zwar WO_4 aber nicht SiO_4 Ionen vorkommen können. Das würde also heissen, dass zwar BeO_4- Tetraeder (Phenacit) und BO_4- Tetraeder (Danburit) als mit den SiO_4- Gruppen gleichberechtige physikalische Baugruppen in den Silikaten existieren, nicht aber LiO_4- Tetraeder im Wolframat denen hier nur geometrische Bedeutung zukäme." These statements are shown in the Fig. too. The importance of distinguishing in crystals between complex anions in physical sense and complex groups merely in geometrical sense has been treated by the author in Part I of his paper concerning the role and significance of the complex anionic potentials in the geochemistry (*Grasselly*, 1959b).

f) The distribution of the complex anions in Fig. 2 in function of the anionic potentials and the electrostatic energies in some relations may be connected with the geochemical classification of the sediments too.

Goldschmidt on the basis of the cationic potentials divided the cations in three groups. Elements with lower ionic potential than 3, such the alkalies and alkaline-earth metals, are soluble and therefore they remain in solution during the weathering and the following transportation; elements of ionic potential between 3 and 12 are the characteristic elements of the hydrolysates and finally the elements with still higher ionic potentials form soluble complex oxyanions, e. g., S^{6+}, P^{5+}, C^{4+}, B^{4+}, N^{5+}.

Szádeczky-Kardoss (1955) in his book „Geochemistry" has pointed out that, though it was noted by *Goldschmidt* that the complex anions of the third groups mentioned above are characteristic partly of the resistates and partly of the evaporates — that is partly as components

of the minerals mostly resistant to the weathering and partly as components of sedimentary rocks, of minerals which are more soluble — however, this contradictory behaviour of the complexes of elements belonging to the same group, on the basis of the ionic potentials, was not yet satisfactorily interpreted.

Szádeczky-Kardoss pointed out that this interpretation may be given on the basis of the complex anionic potentials, since the minerals containing complex anions with highest anionic potentials, are most resistant to the weathering and therefore they become the minerals and complex anions, resp., characteristic of the resistates, whereas the greater part of complex anions — as the ionic potential during the complex-formation considerably diminishes compared with the corresponding cationic potentials — in the sediments will be separated with soluble cations of lower ionic potentials, forming the groups of evaporates and reduzates.

Further he dealt with the geochemical classification of the sediments on the basis of the compound potentials. In the following in connection with the problem of the geochemical classification of the sediments merely on the basis of the complex anionic potentials, without intending to go into a detailed discussion, the aim is to complete *Szádeczky-Kardoss*'s opinion with some contributions shown in Fig. 2.

Starting from the statement of *Rankama* and *Sahama* (1952) that the geochemical classification of sediments is not categorical, since the sedimentation processes are continuous and therefore the sediments of different types are usually mixtures of sediments belonging to two or three groups, it can be expected that neither on the basis of the cationic potentials nor on that of the complex anionic potentials is possible such an arrangement, such a sharp delimitation of the groups of elements and their corresponding complex anions, respectively, which would be characteristic only of the one or of the other group of the sediments.

For example PO_4^{2-} may occurs not only in the resistates (apatite, monacite, xenotime) but also in the hydrolysates (reprecipitated calcium-phosphate) and in phosphate sediments too. The AsO_4^{3-}, SbO_4^{3-}, VO_4^{3-} complex anions may be found in oxidate and hydrolysate sediments, similarly the Ga occurs partly in hydrolysates and partly in oxidates, Sn is secondarily enriched partly in resitates, (cassiterite), partly in Al-rich hydrolysates. The greater part of the sulphur is deposited in the hydrolysates and a considerably smaller part in the precipitates, but the sulphur occurs in the evaporates too, as gypsum and anhydrite as well as potassium-magnesium sulphates. The boron belongs partly to the resistates (tourmaline) but it occurs also in the hydrolysates, oxidates and evaporates too. Zirconium remains largely in the resistates, however, the hydrolysates also contain it.

Nevertheless, some general features may be established from the connection seen in Fig. 2.

It has been mentioned in this paper that the complex anions, included in Fig. 2, can be approximately divided into two groups. Also it is known that the division of the structures to anisodesmic, mesodesmic and isodesmic groups takes place on the basis of the *Pauling*'s electrostatic

valence. The electrostatic valence *(V)* is the charge *(z)* of the central cation divided by its coordination number *(n)*:

$$V = \frac{z}{n}.$$

The structures, wherein bonds with electrostatic valence $V > 1$ (that is greater than the half of the charge of the anion) can be distinguished, are anisodesmic structures with discrete complex anions. The bonding within these anions are therefore stronger than the bonding between the complex anion and the neighbouring cations. In the former bonding a significant covalent character is revealed, whereas the latter is rather ionic. Characteristic anions are: NO_3^{1-}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, ClO_4^{1-} etc.

The structures with bonds the electrostatic valence of which is but the half of the charge of the oxygen, i. e., $V = 1$, are mesodesmic structures and the characteristic anions are firstly the SiO_4^{4-}, GeO_4^{4-}, BO_3^{3-} that is the characteristic anions of silicates, germanates and borates.

Finally, if in the given structure every bonding is weaker than the half of the charge of the oxygen, that is if $V < 1$, in such isodesmic structure discrete groups of ions in general can not be distinguished.

We have no intention to go into a detailed discussion of *Wickman*'s investigations which are summarized in the work of *Rankama* and *Sahama* (1952), but we are only to refer to the following. According to *Wickman*'s results the distribution of elements between sea water and the hydrolysates depends upon the crystal structure of their hydroxides. From the point of view of our present task the following are of importance cited according to *Rankama* and *Sahama* (1952): „If the electrostatic valence from the polarizing cation to the hydroxyl group is less than $\frac{1}{2}$, the charge of the oxygen will not show any tetrahedral splitting. Ionic bond is formed, and the hydroxide is readily soluble. If the electrostatic valence is $\frac{1}{2}$, one of the negative half-charges of oxygen will be occupied; and if the electrostatic valence is 1, two halves of the negative charge are required to bind the hydroxyl group to the cation. In these cases there remain unattached negative charges, which form hydroxyl bonds with the positive charges. If the electrostatic valence greater is than 1, a hydrogen bond is formed which is weak enough to cause the formation of a soluble complex anion."

Consequently taking into consideration the crystal structure of the hydroxides of elements, according to *Wickmann* ionic bonds are formed if $V < \frac{1}{2}$, hydroxyl bonds are formed if $\frac{1}{2} \leqq V \leqq 1$ and finally hydrogen bonds are formed if $V > 1$.

The change of the electrostatic valence, from which the conclusions mentioned above may be drawn, may be also observed in Fig. 2.

In Fig. are denoted that the single cations and their complexes, respectively, of what sediments are characteristic (R = resistates; H =

= hydrolysates; O = oxidates; P = precipitates; E = evaporates). It is to be seen that the single types actually can not be separated from each other. Nevertheless, the two groups distinguishable from crystallochemical viewpoint still show some regularity also from the point of view of the geochemical classification. Namely, the distribution of the elements and their corresponding complexes, respectively, in the function of the complex anionic potentials and the electrostatic energies, supports *Szádeczky-Kardoss*'s assumption that the complexes with higher anionic potential are characteristic rather of the resistates, whereas the complex anions with lower anionic potentials are characteristic rather of the evaporates and partly of the oxidates and precipitates. As it can be seen, among the complex anions deposited in the hydrolysates equally occur complex anions of both higher and lower anionic potentials. It is known that the resistates and hydrolysates are transported as particles of varying size suspended in solution, also in solid state, whereas the oxidates, precipitates and evaporates are deposited from material transported in ionic or colloidal solution to the site of deposition. The minerals of the evaporates, oxidates and precipitates are mostly of anisodesmic structure and the complex anions characteristic of these structures are the most stable ones and the bonding with expressed covalent character within these anions are stronger than the bonding between the complex anion and the surrounding cations. Thus, this bond can be relatively readily broken up and the compound dissolved and dissociated to cation and complex anion can be transported in ionic solution and under altered physicochemical conditions can be redeposited. On the contrary, the complex anions characteristic of the resistates (or hydrolysates) are less stable related to the groups of complex anions above-mentioned, and they are partly characteristic of mesodesmic structures. In the structure of such minerals within the complex anion, and between the complex anion and neighbouring cations, in the strength of these bondings, there are no such considerable differences (being the electrostatic valence of the bond within the complex anion equal even with the half of the charge of the oxygen, i. e., V = 1) as in the case of the anisodesmic structures, especially taking into consideration the main component of the resistates, that is the quartz, in the lattice of which the bonds are approximately of the same character and strength. Therefore, on weathering, these bonds do not break up so readily and the compounds, the minerals characteristic of the resistates or hydrolysates will be rather only mechanically disintegrated and in solid state transported and deposited as resitates or hydrolysates.

SUMMARY

To demonstrate the change of the complex anionic potentials and other values characteristic of ions in the periodic table, that of *Szabó* and *Lakatos* was used, because the separation of the subgroups, the clear demonstration of relationships both horizontally and vertically among the elements by this system, offer the possibility of a more distinct study of the change of ionic potentials and the complex anionic potentials as

well as that of the energy constants and the electrostatic energies in the periodic system.

On representing the values of anionic potentials of the different tetrahedral oxyanions in function of the electrostatic energies, computed on the basis of simple ionic model, the complex anions are arranged corresponding to the place of their central cation in the periodic system, that is on representing the correlation between the two values mentioned, essentially the periodic system is obtained, as it can be seen in Fig. 2. The arrangement of the complex anions gives clear informations partly from the stability relations of the tetrahedral oxyanions as well as the simple possibility of comparing the relative stabilities of the complexes is offered. Further, information is furnished concerning the peculiarities and behaviour of these anions also from chemical and crystallochemical viewpoint, inasmuch as two groups of the complexes may be distinguished. The complex anions with lower anionic potential than 1 in general are stable and are present also in aqueous solution as complex anions and are not dissociated into ingredient ions and are mostly characteristic of anisodesmic structures, on the other hand, the complex anions with higher complex anionic potential than 1 are no longer so stable, in silicate melt, however, they can be present as independent tetrahedral complexes.

The change of the *Pauling*'s electrostatic valence of the bonds within the complex anions may also be seen in Fig. 2.

The distribution of the complex anions represented in Fig. 2 in some relations may be connected with the geochemical classification of the sediments too. Though, neither on the basis of the cationic potentials nor on that of the complex anionic potentials is possible such an arrangement, such a sharp delimination of groups of elements and their corresponding tetrahedral oxyanions respectively, which groups would include elements characteristic only either of the one or of the other group of sediments, nevertheless, some general features may be established from the connection seen in Fig. 2.

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